Electro-Fenton oxidation of imidacloprid by Fe alginate gel beads

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ABSTRACT

This study describes the removal of imidacloprid by a heterogeneous electro-Fenton system with iron alginate gel beads (EF-FeAB). The effects of the initial pH and initial concentration of alginate beads (FeAB) on the imidacloprid removal rate were studied. The removal efficiency was maintained with an increase in Fe dosage and decreased with an increase in the initial pH. The optimum dose of iron alginate gel beads (FeAB) was found to be 1.3 mM, and complete imidacloprid removal was observed within 120 min at an initial pH of 2. A kinetic analysis showed that the removal of imidacloprid by EF-FeAB followed a first-order kinetics model. Because complete mineralization was the primary goal, the main degradation routes of imidacloprid were proposed on the basis of LC–MS data. Finally, the process was implemented in continuous mode with FeAB in a stirred-tank reactor. High imidacloprid removals of 80% and 90% were achieved by operating for residence times of 2 and 4 h, respectively. The process ran continuously without operational problems, and the particle shapes were maintained throughout the oxidation process.

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1. Introduction

Pesticides are used for controlling, repelling, preventing or eradicating pests and include not only a wide range of chemical compounds but also antimicrobial or disinfectant agents. According to the active chemical groups, the main categories of pesticides are as follows: organochlorines, organophosphates, organosulfurs, carbamates, formamidines, dinitrophenols, pyrethroids, nicotinoids, spiosinas, phenylpyrazoles, pyrroles and pyrazoles, among others. Despite their positive effects in agriculture, their compositions often pose a threat to humans and the environment [1].

Pesticide production and application have progressively increased worldwide during recent decades. Among these compounds, imidacloprid [1-(6-chloro-3-pyridylmethyl)-N-nitro-imidazolidin-2-ylideneamine] is a widely used insecticide introduced for agricultural use in the 1990s, and it is mainly used at the present to control sucking insects in crops (e.g., aphids, leafhoppers, thrips, whiteflies and termites) [2,3]. Imidacloprid belongs to the nicotinoid chemical family. Because of their molecular shape, size, and charge, nicotinoids fit into receptor molecules in the nervous system that normally receive the molecule acetylcholine. Imidacloprid and other nicotinoids irreversibly block acetylcholine receptors. Therefore, imidacloprid is toxic to some species of aquatic animals at extremely low concentrations [2]. In addition, according to the EPA, the high solubility of imidacloprid along with its mobility and potential to leach into ground water are concerns during its transport to surface water in dissolved runoff [4].

More and more xenobiotics are being detected in the environment all the time, especially pesticides. To address the pollution of agricultural wastewater by pesticides, various treatment processes have been studied, namely physical treatments (lined evaporative beds and activated carbon adsorption), chemical treatments (photolysis, hydrolysis and chemical oxidation) and biological treatments (bacterial degradation) [5–7].

Different advanced oxidation processes (AOPs) have proven to be powerful oxidative techniques for treating several organic pollutants such as pesticides [8–12]. AOPs are based on the in situ generation of hydroxyl radicals ($^{\bullet}$OH), a highly powerful oxidizing agent. Among these processes, Fenton and electro-Fenton techniques have attracted attention from investigators around the world. These processes are based on the oxidation of ferrous iron to ferric iron by hydrogen peroxide (Eq. (1)), releasing a hydroxyl radical with the capacity to oxidize contaminants.

$$Fe^{2+} + H_2O_2 \rightarrow {}^{\bullet}OH + Fe^{3+} + OH^- \tag{1}$$
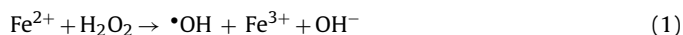
The electro-Fenton process uses electric current for the in situ generation of H_2O_2 by O_2 reduction in the presence of dissolved Fe^{2+}. Furthermore, the overall process does not create secondary pollutants because there is a catalytic cycle with Fe^{3+} species in the medium that revert to Fe^{2+} by different reduction processes, which involve H_2O_2 or organic intermediate radicals, as well as the direct reduction of Fe^{3+} on the cathode. Therefore, the weight of the added ferrous iron (II) is much smaller than it is in the traditional Fenton method [13].

Hence, the electro-Fenton process offers the advantage of avoiding the continuous addition of H_2O_2, which is an unstable and potentially harmful compound. In addition, iron recycling reduces Fe precipitation at high pH values and the formation of Fe sludge [13]. Several studies have concluded that the electro-Fenton process is more economical, efficient and environmentally friendly for removing organic matter than other conventional processes [14–20]. In recent years, electro-Fenton processing has been shown to be an effective alternative for the removal of several substances such as refractory organic compounds from stabilized landfill leachate [21], photographic processing wastewater [22], cephalexin [23], atrazine [24] and flumequine [25]. In addition, pesticides were also treated with Fenton processes [26–29] to good effect. Zhao et al. [30] degraded the pesticide imidacloprid by employing a $Fe_3O_4@Fe_2O_3$/activated carbon aerogel cathode within a wide range of pHs, leading to 90% removal after 30 min of treatment.

The main drawbacks in Fenton or electro-Fenton processes are that the use of dissolved iron as a catalyst requires its subsequent removal from treated water, mostly as iron oxyhydroxide sludge. For this reason, significant efforts have been made in recent years in the field of heterogeneous catalysis to facilitate the reuse of iron [31–34]. Among the different catalysts used in heterogeneous Fenton reactions, iron alginate gel beads (FeAB) have shown high catalytic activities for the oxidation of organic compounds, with minimal iron leaching [35–38]. Their immobilization in biopolymer matrix beads is a simple, inexpensive and effective technique [37] that permits their operation within a wide range of pHs. Furthermore, FeAB can be continuously reused in batch or continuous mode for the treatment of synthetic dyes [36,37].

This study focuses on the applicability of FeAB as a heterogeneous electro-Fenton catalyst in the degradation of imidacloprid. The efficiency of the electro-Fenton method with iron alginate gel beads (EF-FeAB) was studied through the reduction of imidacloprid and the characterization of imidacloprid transformation products by LC–MS. Finally, the reusability of this catalyst was shown in continuous mode experiments under ideal operational conditions.

2. Experimental

2.1. Imidacloprid solution

Imidacloprid solution ($100\,mg\,L^{-1}$) was prepared using an imidacloprid-grade Pestanal analytical standard provided by Sigma–Aldrich (Barcelona, Spain).

2.2. Iron alginate gel beads (FeAB)

A 2.0% (w/v) sodium alginate solution was purchased from Sigma–Aldrich (Barcelona, Spain) and dropped through a syringe into hardening solution composed of $0.05\,M\;Fe^{3+}$ (Fe_2SO_3, Sigma–Aldrich (Barcelona, Spain)) to create spherical alginate beads loaded with Fe [37]. These particles were cured at $4\,°C$ for 2 h in the gelling solution, then filtered and washed repeatedly with distilled water. Finally, they were stored at $4\,°C$ in distilled water for the degradation study.

2.3. Batch electrochemical reactor set-up

Several batch experiments were completed in an electrochemical cell with a working volume of 0.15 L. The cathode was formed from a graphite sheet (Carbon Lorraine, France) and a Boron-Doped Diamond (BDD) (DiaChem, Germany) electrode was used as an anode. Both portions were connected to a direct current power supply (HP model 3662). The electrodes (surface $11\,cm^2$) were placed in opposition to each other with an electrode gap of 6 cm. A constant

potential drop of 5 V was applied with a power supply (HP model 3662). This value was shown to be optimal by Iglesias et al. [35]. The process was monitored with a multimeter (Fluke 175). The reactor was filled with imidacloprid solution at the desired pH. The solution was agitated with a magnetic stirrer to avoid concentration gradients.

During the electro-Fenton process (Fig. 1A), a continuous bubbling ($1\,L\,min^{-1}$) of air at atmospheric pressure was maintained in the reactor around the cathode; this flow started 10 min before the electro-Fenton process to reach a stationary O_2 concentration. This bubbling was carried out for the *in situ* generation of H_2O_2 by the electrochemical reduction of oxygen [39]. Under this configuration, different experiments were carried out using free and immobilized Fe ion (FeAB) systems according to the selected concentration of Fe.

2.4. Sample preparation and preservation

For all experiments, 1 mL samples were taken periodically from the reactor to be analyzed for pH, pesticide concentration and degradation product identification. The samples were saved in hermetically sealed glass vials and protected from light. Vials were stored at $4\,°C$ until the analysis.

2.5. Imidacloprid analysis

The sample imidacloprid concentrations were determined by HPLC (Agilent 1100) equipment with an XDF-C8 reverse-phase column ($150\,mm \times 4.6\,mm$ i.d., $5\,\mu m$). Prior to injection, the samples were filtered through a $0.45\,\mu m$ Teflon filter. The injection volume was set at $20\,\mu L$, and an isocratic eluent (50:50 acetonitrile/water) was pumped at a rate of $1\,mL\,min^{-1}$ for 5 min. Detection was performed with a diode array detector at 270 nm, and the column temperature was maintained at room temperature.

To identify the transformation products obtained in the imidacloprid degradation, several samples were analyzed with HPLC–MS (Agilent 1100) equipment with an LC column Luna $5\,\mu$ C18 100A. The samples were filtered through a $0.45\,\mu m$ Teflon filter before injection. In this case, the isocratic eluent was 98% (1 nM aqueous sodium formiate and 0.1% formic acid) and 2% (acetonitrile and a 0.1% of formic acid) that was pumped at a rate of $0.4\,mL\,min^{-1}$ for 40 min. Detection was carried out with a diode array detector at 220 nm and the column temperature was maintained at $35\,°C$. The coupled mass spectrometer was a Hewlett-Packard 5989B with a detection range from 10 to 2000 Da.

2.6. Kinetic studies

Kinetic studies were conducted to model the EF-FeAB behavior. The imidacloprid concentration profiles were fitted by using a suitable kinetic equation and the rate constants were calculated by using SigmaPlot 4.00 (1997) software. The SigmaPlot curve fitter uses an iterative procedure, based on the Marquardt–Levenberg algorithm, which seeks the values of the parameters that minimize the sum of the squared differences between the observed and predicted values of the dependent variable.

2.7. Continuous reactor of EF-FeAB process set-up

An electrochemical cell with the same characteristics as the one used for the batch experiments was employed (Fig. 1B). The electro-Fenton reactor had a working volume of 0.15 L with 4.27 g of FeAB and a working pH value of 2. The H_2O_2 was produced electrochemically by bubbling compressed air near the cathode at approximately $1\,L\,min^{-1}$. The pesticide solution was homogenized by a magnetic stirrer. A dual-headed peristaltic pump was used to maintain a
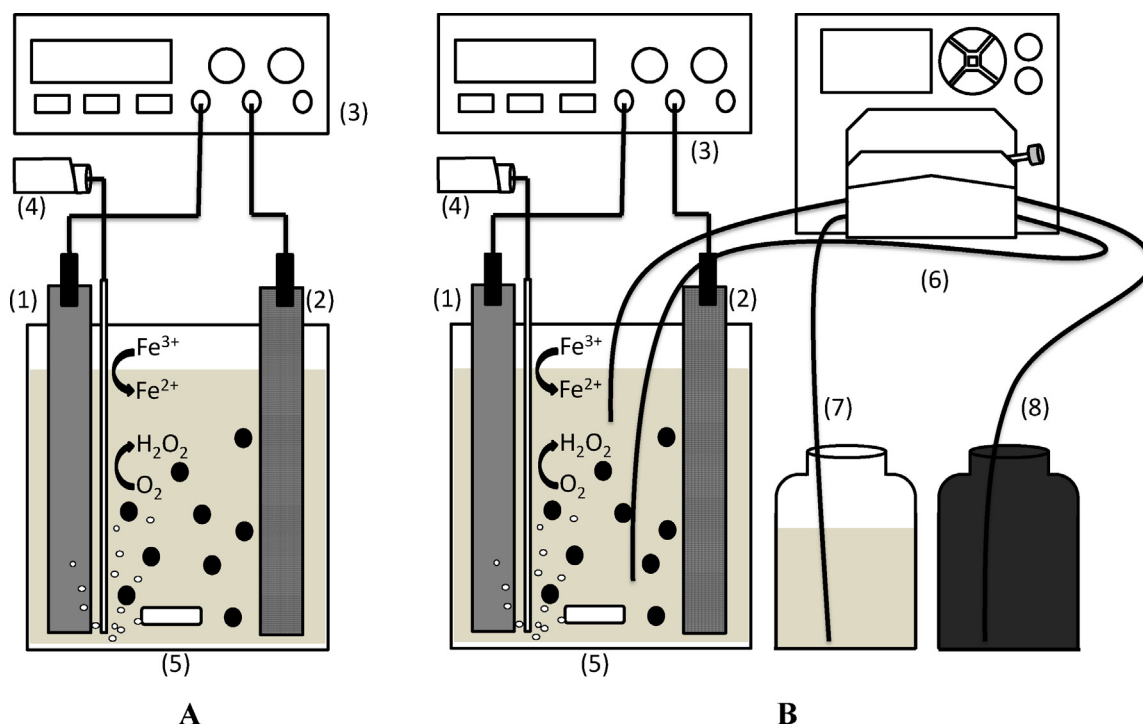
Fig. 1. Schematic diagram of electro-Fenton experimental set-up in batch processing. (A) Graphite sheet acting as cathode (1), BDD electrode acting as anode (2), power supply (3), air supply (4), magnetic stirrer (5); and continuous process. (B) Graphite sheet acting as cathode (1), BDD electrode acting as anode (2), power supply (3), air supply (4), magnetic stirrer (5), dual-headed peristaltic pump (6), outlet flow (7), inlet flow (8).

continuous flow of pesticide solution through the reactor. Thus, the reactor behaved as a continuous stirred-tank reactor (CSTR). The inlet solution and the reactor were kept in darkness. Samples from the outlet flow were frequently taken to measure the pH and analyze the pesticide concentration. The reactor operated in continuous mode at residence times of 2 h and 4 h.

An expression that relates the degradation and residence times was obtained on the basis of the CSTR hydrodynamic behavior and the first order kinetic model. It is shown in Eq. (2).

$$D = 100 \cdot \frac{k \cdot \tau}{1 + k \cdot \tau} \qquad (2)$$

where D is the % of degradation, k is the previously observed kinetic coefficient for the first order reaction (min^{-1}) and τ is the residence time (min).

3. Results and discussion

3.1. Comparing different EAOPs and their kinetics

Different electrochemical processes were carried out in an electrochemical reactor with a graphite sheet electrode as the cathode and a BDD electrode as the anode. Although graphite sheet electrodes have been used in previous studies [35,37] for dye decolorization with satisfactory results, BDD electrodes have proven to be very powerful anodes [40,41]. The oxidation power of BDDs can be explained in the following terms: (i) BDD has a large O_2-evolution overpotential, which promotes the formation of hydroxyl radicals in large amounts, and (ii) hydroxyl radicals are physisorbed on BBD surfaces and are therefore more available to react with organics. A remarkable example of the outstanding oxidation power of this anode was reported by Oturan et al. [24].

In this study, the degradation of imidacloprid by using the electro-Fenton process with free and immobilized Fe ions (EF-FeAB) as well as the electrochemical process was tested in an

electrochemical batch reactor. A pH of 2 and a potential drop of 5 V were selected in response to our previous study [35]. The electro-Fenton process was found to be significantly more efficient in the degradation of imidacloprid than the electrochemical process (Fig. 2) because the electro-Fenton process adds the effect of the Fenton reagent, which is electrochemically generated *in situ*.

Better EF-FeAB process performance can be observed in comparison to the electro-Fenton process with free iron. This finding can be explained because Fe^{3+} precipitates when pH increases and the dissolved iron concentration is reduced. As shown in Fig. 2, the oxidation rate of imidacloprid in the presence of FeAB was slightly higher than the one obtained with free iron, resulting in
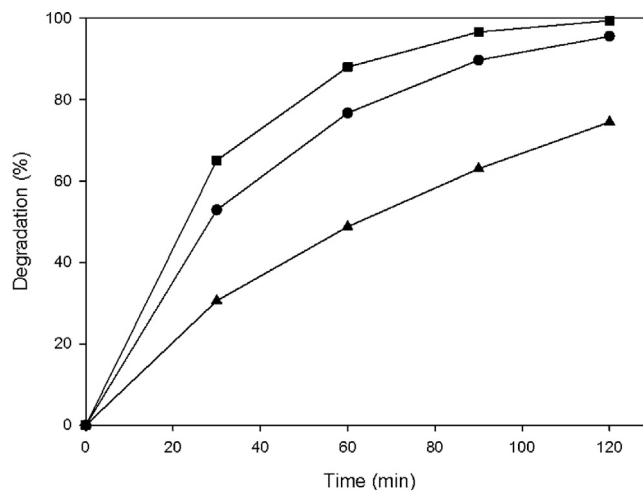
Fig. 2. Percentage of imidacloprid degradation under several AOPs: electrochemical process (▲) (working volume of 0.15 L, potential drop 5 V and pH 2); electro-Fenton treatment (●) (150 mg L^{-1} of iron, working volume of 0.15 L, air flow 1 mL min^{-1}, potential drop 5 V and pH 2); and EF-FeAB (■) (4.27 g of FeAB, working volume of 0.15 L, air flow 1 mL min^{-1}, potential drop 5 V and pH 2).
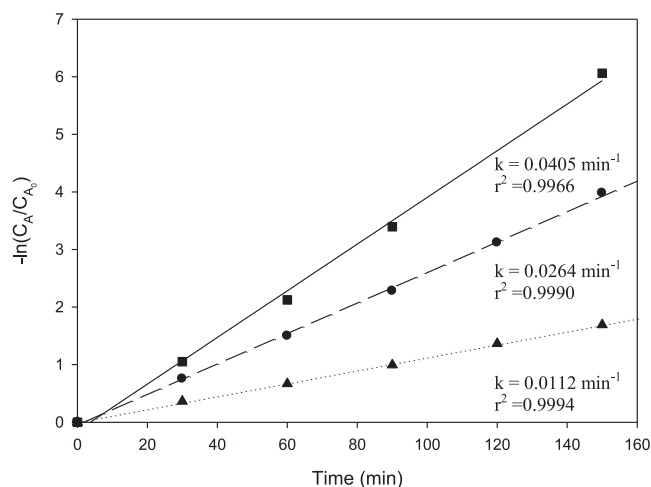
Fig. 3. First-order kinetics (ln normalized imidacloprid concentration (C_A) remaining *vs.* time) of imidacloprid degradation by electrochemical processing (▲, dotted line) (working volume of 0.15 L, potential drop 5 V and pH 2); electro-Fenton treatment (●, long dash line) (150 mg L^{-1} of iron, working volume of 0.15 L, air flow 1 mL min^{-1}, potential drop 5 V and pH 2); and EF-FeAB (■, solid line.) (4.27 g of FeAB, working volume of 0.15 L, air flow 1 mL min^{-1}, potential drop 5 V and pH 2). Symbols represent the experimental data and line up with the first-order kinetic model.

degradation values of 95% and 90% at the end of the treatment, respectively.

Kinetic studies of the three assayed processes were carried out. In these experiments, the reaction kinetics were investigated and the regression coefficients for zero, first and second-order reactions were calculated. The results indicated that the degradation of imidacloprid under all the different assayed EAOPs could be quantitatively described by a first-order kinetic equation (Eq. (3)) with respect to the pesticide concentration as follows:

$$\frac{dC}{dt} = -kC \qquad (3)$$

where C, concentration of imidacloprid (mg L^{-1}); t, reaction time (min); and k, kinetic coefficient for the first order reaction (min^{-1}). The rate constant values and statistical correlation parameters are shown in Fig. 3. As expected from the degradation profiles, the k values indicate that the decrease in concentration with time is faster under the EF-FeAB process (k = 0.0445 min^{-1}) and that the slowest degradation predictions are those related to the electrochemical process (k = 0.0112 min^{-1}). These results are in accordance with other studies performed on the photocatalytic degradation of imidacloprid, which employed different states of the catalyst TiO$_2$ to demonstrate its first-order degradation kinetics [42–45]. However, it is worth mentioning that the first-order rate constants calculated in this study differ in comparison to several photocatalytic studies. For example, Žabar [44] studied the photocatalytic degradation of imidacloprid, thiamethoxam and clothianidin by employing a tailor-made photoreactor with six polychromatic fluorescent UVA lamps and immobilized titanium dioxide (TiO$_2$) on glass slides. They determined that within 2 h of photocatalysis, all three neonicotinoids were degraded following first order kinetics, with a rate constant k = 0.035 min^{-1} for imidacloprid. This value is lower than that obtained in the EF-FeAB process developed in this work (k = 0.0445 min^{-1}). These results suggest that imidacloprid is rapidly and efficiently degraded by EF-FeAB in comparison to photocatalytic treatments [44,45].

3.2. Effects of FeAB dosage

As mentioned in the literature [46–50], several polymer network gels could be used for the removal of inorganic and organic
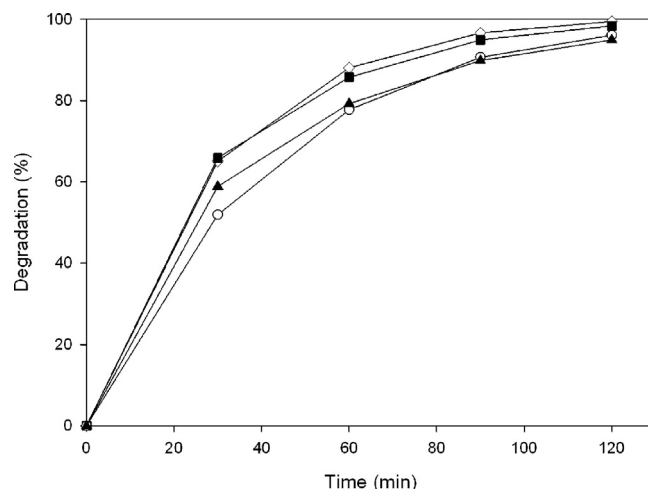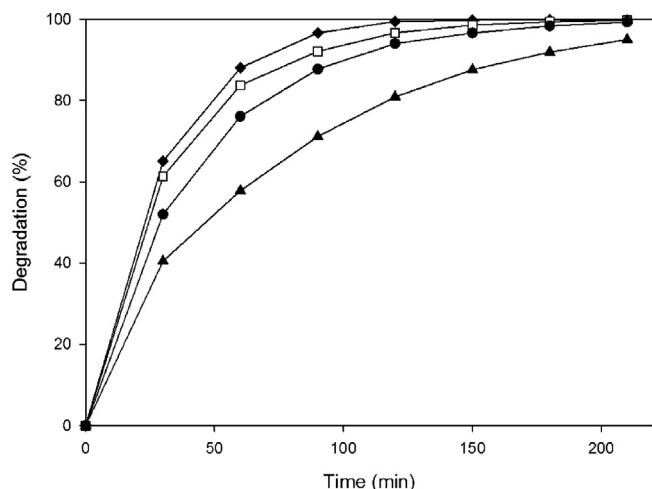

Fig. 4. Effect of FeAB on imidacloprid degradation by electro-Fenton treatment with a working volume of 0.15 L, air flow 1 mL min^{-1}, potential drop of 5 V and pH of 2. Symbols: 4.27 g (◇), 8.54 g (■), 12.81 g (○) and 16.84 g (▲).

contaminants present in wastewater. Furthermore, the use of this type of gels has already been studied as a catalyst in electro-Fenton reactions [35–37]. Rosales et al. [37] evaluated the removal of some typical dyes, such as lissamine green B and azure B, by using iron alginate gel beads as catalysts for the electro-Fenton process, reaching a 98–100% removal in successive batches and a 97–98% of decolorization in a continuous bubble reactor with a residence time of 30 min. Taking into account these previous studies, EF-FeAB was assayed for its degradation of imidacloprid by evaluating the effect of the FeAB load on the electrochemical reactor. Thus, the EF-FeAB was carried out with 4.27, 8.54, 12.81 and 16.84 g of FeAB (corresponding with 1.3, 2.6, 3.9 and 5.2 mM of Fe, respectively) at pH 2, a potential drop of 5 V and an air flow of 1 L min^{-1}. Fig. 4 shows the percentage of imidacloprid degradation with time by EF-FeAB at different FeAB weights. Notably, the removal of pesticide from the solution was faster with lower FeAB weights, and greater than 95% degradation was detected in all cases after 2 h of treatment. For this reason, the effect of the loaded FeAB on the reactor, at least within the studied range, is low. Therefore, the iron concentration necessary for this process is the one contained in 4.27 g of FeAB. The increased FeAB content did not provide positive effects; on the contrary, a delay in imidacloprid oxidation rates was observed when the weight of the beads was increased in the medium. The FeAB increase in the medium reduced the current intensity; therefore, the reactions over the electrodes were reduced as well. As a result, 4.27 g of FeAB was the chosen weight for studying other variables such as the pH.

3.3. Effect of solution pH

The efficacy of the Fenton reactions depends on the pH; therefore, its impact on the catalytic activity of FeAB was studied for imidacloprid degradation. For this purpose, several experiments were performed at pH 2, 3, 5 and 7 containing 4.27 g FeAB (Fig. 5).

As shown in Fig. 5, there is a clear pH effect over the EF-FeAB degradation of imidacloprid. This finding is in agreement with the optimal value for the Fenton treatment as reported by Iglesias et al. [35]. As shown in Fig. 5, degradation is faster at the lowest pH, and good results are attained at pH 3 and even at pH 7. At pH 7, more than 90% imidacloprid degradation was obtained after 200 h. Therefore, the electro-Fenton process is efficient at a neutral pH

Fig. 5. Effect of pH on imidacloprid degradation by EF-FeAB with a working volume of 0.15 L, air flow of 1 mL min^{-1}, potential drop of 5 V and 4.27 g of FeAB. Symbols: pH 2($\blacklozenge$), pH 3($\square$), pH 4 ($\bullet$) and pH 7 ($\blacktriangle$).

with a slow reduction in the degradation rate. Even if no iron sludge is produced because of its immobilization on alginate beads, reactions are much more favorable under acidic conditions as described by Zhao et al. [30]. The pH affects the speciation of iron ions and the decomposition of H_2O_2 into O_2 and H_2O [51]. In addition, the oxidation potential of hydroxyl radicals was reduced at higher pH values from $E_0 = 2.8$ V to $E_{14} = 1.96$ V [52].

Hydrogen peroxide decomposition produces a slower degradation at higher pH values; nevertheless, the continuous electrogeneration of H_2O_2 by means of aeration maintains its concentration in the medium. Consequently, the degree of imidacloprid depletion after longer periods of treatment is very similar at a pH between 2 and 7. Moreover, Rosales et al. [37] previously reported that the ionic cross-links between the carboxyl group on the alginate chains and the Fe ions prevents the formation of Fe(OH)$_3$ and eliminates the negative effect of iron sludge generated by the classic Fenton oxidation process at higher pH values. Hence, the FE-FeAB has good degradation behavior for the treatment of effluents containing the pesticide imidacloprid within a wide pH range.
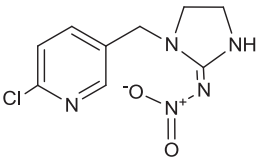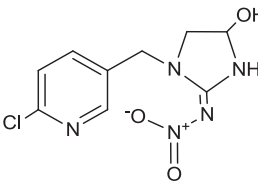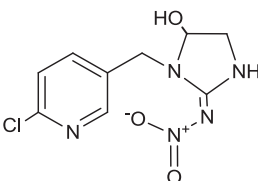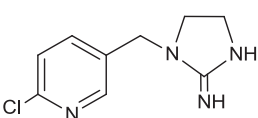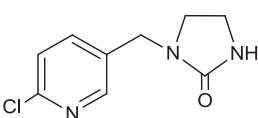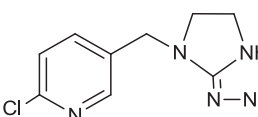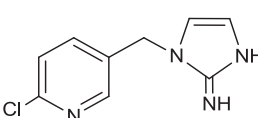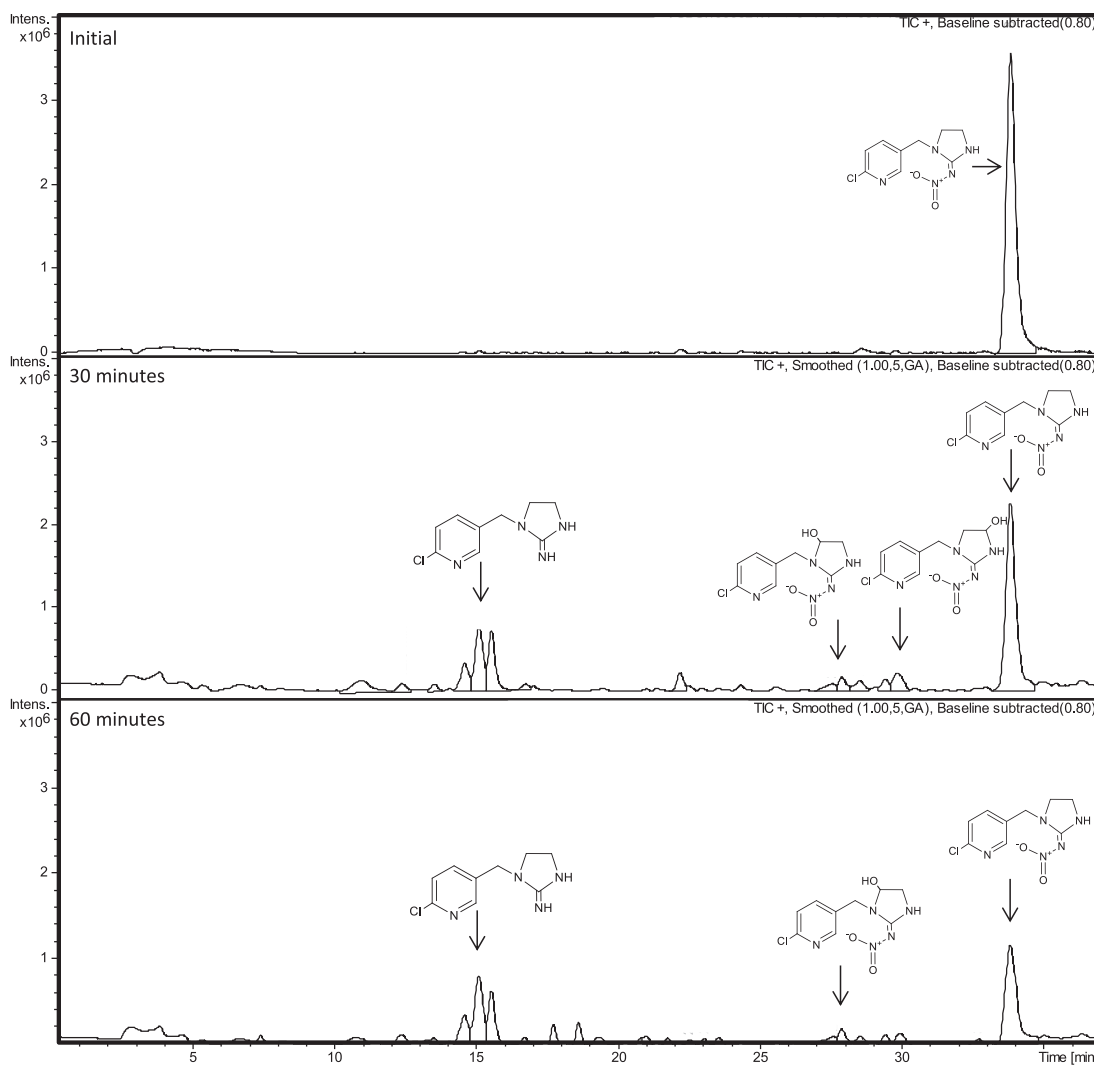

Fig. 6. LC–MS profile of imidacloprid in an EF-FeAB treatment with a working volume of 0.15 L, air flow of 1 mL min^{-1}, potential drop of 5 V, pH 2 and 4.27 g of FeAB at different treatment times (initial, 30 min and 60 min).

Table 1
LC–MS identification of the chemical structure, retention time and main mass fragmentation values of identified imidacloprid intermediates formed during the EF-FeAB process.

| Identification number	Compound	Formula	Structure	Retention time (min)	Main mass fragmentation value (m/z)
1	Imidacloprid	$C_9H_{10}ClN_5O_2$		33.8	278
2	4-Hydroxy derivative	$C_9H_{10}ClN_5O_3$		29.9–27.5	294
3	5-Hydroxy derivative	$C_9H_{10}ClN_5O_3$		29.9–27.5	294
4	Cyclic guanidine derivative	$C_9H_{11}ClN_4$		15.1	211
5	Cyclic urea	$C_9H_{10}ClN_3O$		29.4	234
6	Nitroso derivative	$C_9H_{10}ClN_5O$		27.7	262
7	Olefinic cyclic guanidine	$C_9H_9ClN_4$		20.5	209

3.4. Analysis of imidacloprid degradation compounds

EF-FeAB treatment of imidacloprid solution led to the formation of different intermediate species until the pollutant was completely mineralized. The degradation compounds were identified by LC–MS analysis because it is best suited to detect these compounds [3,53,54].

The identification was based on mass fragmentation values (Table 1) and by comparing the mass spectra to a database. The initial solution and samples from different treatment times at pH 2 and pH 7 were analyzed. The EF-FeAB generates several compounds; however, this study focuses on the main compounds described in Table 1 that have already been identified in several works [3,6,44,55–57]. Fig. 6 shows the LC–MS results at different treatment times and pH 2. Taking into account the intensity of the signal, a decrease in the concentration of

imidacloprid and its derivatives can be observed with treatment time. The final analysis of samples after 24 h of treatment indicated the complete removal of any compounds. As shown in Fig. 5, the imidacloprid degradation profiles from EF-FeAB under higher pH values were much slower. The LC–MS study also allowed for the identification of two intermediates at pH 7 (Table 1 (6) nitroso derivative and (7) olefinic cyclic guanidine) that are not present at pH 2 because of its faster degradation.

The most substantial changes in the imidacloprid molecule were studied according to its intermediates. There are several atoms on the imidacloprid molecule that undergo chemical alterations to create the main degradation compounds as reported by Johnson [58]. Fig. 7 describes the main changes in the imidacloprid molecule that took place to generate the compounds described in Table 1.
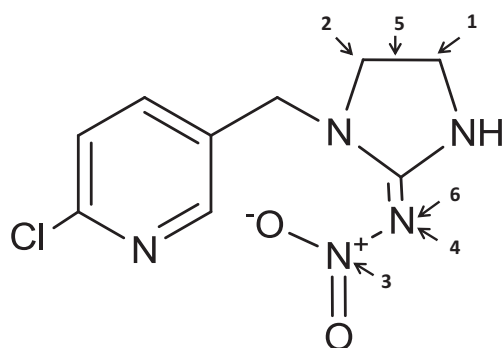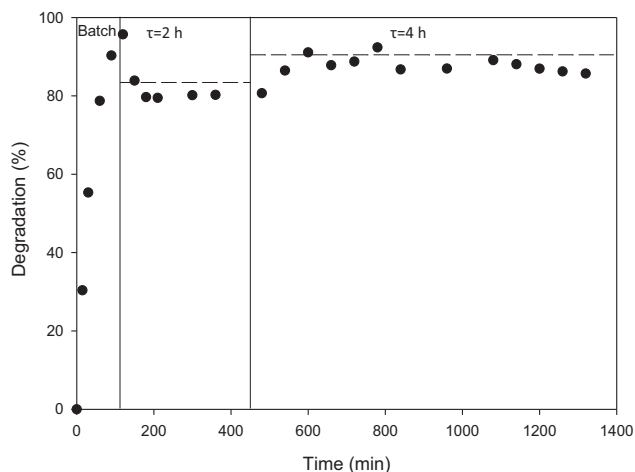
Fig. 7. Main changes in the imidacloprid molecule taking place in the EF-FeAB: (1) $R_2CH_2 \rightarrow R_2C(OH)H$ generation of 4-hydroxy derivative; (2) $R_2CH_2 \rightarrow R_2C(OH)H$ generation of 5-hydroxy derivative; (3) $-N-NO_2 \rightarrow -N-NO$ generation of nitroso derivative; (4) $-N-NO_2$, $-N-NO \rightarrow -N-NH$ generation of cyclic guanidine derivative; (5) $R-CH_2-CH_2-R \rightarrow R-CH=CH-R$ generation of olefinic cyclic guanidine from cyclic guanidine derivative; (6) $-NH$ (from cycled guanidine derivative) $\rightarrow$ $=O$ generation of cyclic urea.


Fig. 9. Degradation profile of imidacloprid by EF-FeAB treatment in batch and continuous modes with a working volume of 0.15 L, air flow 1 mL min^{-1}, potential drop 5 V, pH 2 and 4.27 g of FeAB at different residence times.

From these compounds, a plausible mineralization sequence was proposed for imidacloprid degradation during the EF-FeAB process (Fig. 8). This pathway is in accordance with studies reported by Roberts and Hutson [55] for natural degradation. In addition, many of these compounds are also found in other degradation processes such as microbial degradation in soils [56,57], ozonation [6] and photo-degradation [3,44]. There are several intermediates and by-products of imidacloprid degradation but the reaction velocities are unknown; in this study, a process simplification is shown.

3.5. Continuous mode

Rosales et al. [37] demonstrated the reusability of FeAB in batch and continuous modes of the electro-Fenton process for the decolorization of several dyes. Accordingly, a continuous mode was tested to evaluate the activity and stability of the catalytic action of FeAB and to minimize site requirements for the treatment of large amounts of wastewater. Several imidacloprid treatments with EF-FeAB at different residence times were carried out. In all cases, each steady state was maintained for at least three times the residence time. The process took place in a reactor of similar characteristics to the one used for batch experiments and described in Section 2.7.

Fig. 9 shows the increase of degradation with the residence time, attaining 80% for a residence time of 2 h and 90% for a residence time of 4 h. In addition, the theoretical degradation values were calculated using Eq. (2) for the two employed residence times, and they are represented in Fig. 9 as the long dashed line. The proposed model was able to satisfactorily describe the imidacloprid degradation data and to serve our goal of properly characterizing the kinetics of the remediation process.

Therefore, these experiments confirm that EF-FeAB treatment can be used for real effluents. It is remarkable that the system was able to operate in continuous mode to treat a pesticide such
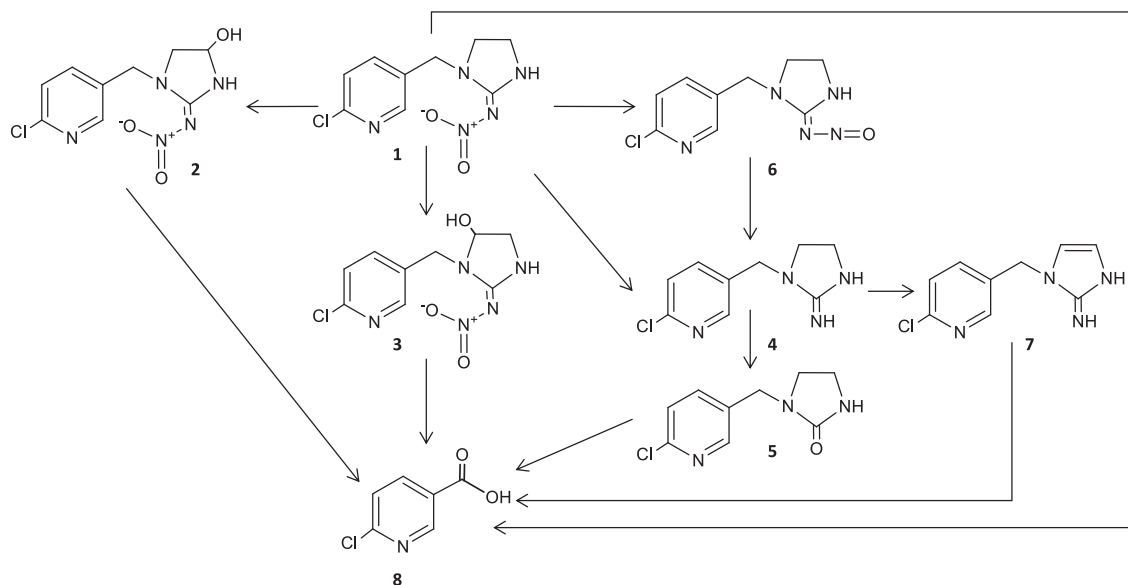
Fig. 8. Plausible degradation pathway of imidacloprid by the EF-FeAB method. (1) Imidacloprid; (2) 4-hydroxy derivative; (3) 5-hydroxy derivative; (4) Cyclic guanidine derivative; (5) Cyclic urea; (6) Nitroso derivative; (7) Olefinic cyclic guanidine; (8) 6-chloronicotinic acid.

as imidacloprid without operational problems and still reach high degradation percentages.

4. Conclusions

In the present work, the electro-Fenton process used FeAB as a catalyst for the degradation of imidacloprid pesticide. The performance of this technique is characterized by the following:

- The EF-FeAB was probed to achieve better degradation results compared to electrochemical degradation and classical electro-Fenton processes.
- The process does not require a high volume of alginate gel beads and it works at several pH values (2–7), and better results are attained under acidic conditions. Furthermore, immobilization prevents iron precipitation at a high pH and its continuous addition.
- It is feasible to use this methodology in a continuous reactor without operational problems.
- The degradation compounds were identified and a plausible degradation pathway was proposed.

The EF-FeAB treatment application proved to be a good degradation method for imidacloprid, which is a widely used neonicotinoid pesticide with known toxicity.

Acknowledgements

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